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ABSTRACT

Submillimeter absorption spectra of nitrogen, nitrogen-argon mixtures, and methane have been measured using temperatures and pressures near to those found in the atmospheres of Titan and Saturn. The experiments show the spectral signature of dimers which will likely appear in far-infrared spectra of Titan that will be obtained by the Composite Infrared Spectrometer (CIRS) onboard the Cassini spacecraft. The recent CIRS spectrum of Jupiter shows far-infrared spectral lines of methane and the corresponding lines are observed in the laboratory. We are extending this work to lower frequencies using a new differential Michelson interferometer that operates over the frequency region 3–30 cm^{-1}.

1. Introduction

We have conducted experiments, and are developing a new spectrometer and absorption cell apparatus, to measure submillimeter spectra of simple gases and gas mixtures. The spectra signatures of dimers is an area of particular interest as these features have been seen in planetary spectra. Dimers are weakly bound pairs of molecules that form stably when the temperature is comparable to the depth of the intermolecular potential. The dimer has a set of vibrational and rotational energy states which depend on the molecules' separation and orientation. Even though the individual molecules that compose the dimer do not possess permanent electric dipole moments, the dimer can possess a dipole moment and transitions between energy states give rise to rotation-vibration spectral lines at low frequencies. The Voyager spectrum of Jupiter shows small H_2-H_2 dimer features located near the S(0) and

S(1) transitions of hydrogen at 354 and 587 cm^{-1} respectively (McKellar 1984; Frommhold, Samuelson, & Birnbaum 1984), and the Voyager spectrum of Titan shows features in the same regions which are attributed to the H_2-N_2 dimer (Borysow & Frommhold 1986).

2. Nitrogen and Nitrogen-Argon Spectra

The left panel of Figure 1 shows a comparison of low temperature N_2 and N_2-Ar absorbance spectra ($-\ln$(transmission)). The measurements were conducted using a Fourier transform spectrmeter and multi-reflection absorption cell cooled with liquid argon or liquid nitrogen (Wishnow, Leung, & Gush 1999). The optical path was 52 m and the spectral resolution was 0.24 cm^{-1}. The upper curve is from 538 Torr of N_2 at 78 K (2.54 Amagat) and the lower curve is from a 50/50 mixture of N_2-Ar at 88 K (2.6 Amagat) (Amagat units are a ratio of sample density to Loschmidt's number, the atmospheric number density at STP). The circles are the calculated absorbance for 2.54 Amagat of N_2 at 93 K based on the previous generation of high pressure, low resolution experimental studies Dore & Filabozzi (1987).

The broad continuum is due to the N_2 collision-induced translation-rotation spectrum. The rippled structure superposed on the continuum is due to the presence of dimers and it is enhanced in the N_2-Ar spectrum relative to the pure N_2 spectrum. The dimer structure can only be observed using relatively high spectral resolution and relatively low gas pressures; this structure was not seen in the previous generation of high pressure experiments.

The right panel of Figure 1 shows N_2-Ar spectra with the collision-induced continuum removed. The N2/Ar mixing ratio, total density, and temperature from top to bottom are: 50/50, 5.2 Amagat, 88 K; 24/76, 3.04 Amagat, 88 K; pure N_2, 2.54, 78 K. The detailed structure in the upper two curves is clearly different from the lower, pure N_2 curve. The amplitude of the ripples is obviously enhanced by the presence of argon; notice that the upper curve and lower curve have the same amount of N_2 in the gas sample. It is interesting that the minima of the ripples correspond to the rotational transition frequencies of the N_2 molecule. At frequencies between 35 and 50 cm^{-1}, the ripples give way to detailed structure indicating that the N_2 molecule is no longer a free rotator for low N_2 rotational states. This work has been reported previously (Wishnow, Gush, & Ozier 1996), and it is compared to calculated N_2-Ar spectra (Wang, McCourt, & Le Roy 2000).

The rippled structure is likely to be observed in the spectrum of Titan by the CIRS spectrometer on Cassini. The argon abundance determined spectroscopically can be compared to mass spectrometer measurements made by the Huygens descent probe.

3. Methane

Even though the methane molecule is symmetric in the electronic and vibrational ground state, a weak dipole moment arises in a molecule with rotational quantum state $J > 0$ due to centrifugal distortion. Figure 2 shows the first observation of centrifugal distortion spectral lines below 80 cm^{-1}. Early CIRS spectra of Jupiter, courtesy of Don Jennings NASA/GSFC, show methane lines in absorption over the range 60 to 110 cm^{-1}. The analysis of the laboratory data is underway to support the interpretation of Jupiter spectra and the anticipated data from Saturn.

4. New Spectrometer System

We are developing a new differential Michelson interferometer to study dimer spectra in the frequency region 3–30 cm^{-1}. The system has twin light pipe optical cells 6.11 m long and two ^{3}He cooled bolometers. Each detector measures the interferogram that arises from the difference spectrum of cell 1 and cell 2. In principle, if both cells contain the same quantity of N_2 and argon is added to one cell, the interferogram should be due only to the N_2-Ar dimers.

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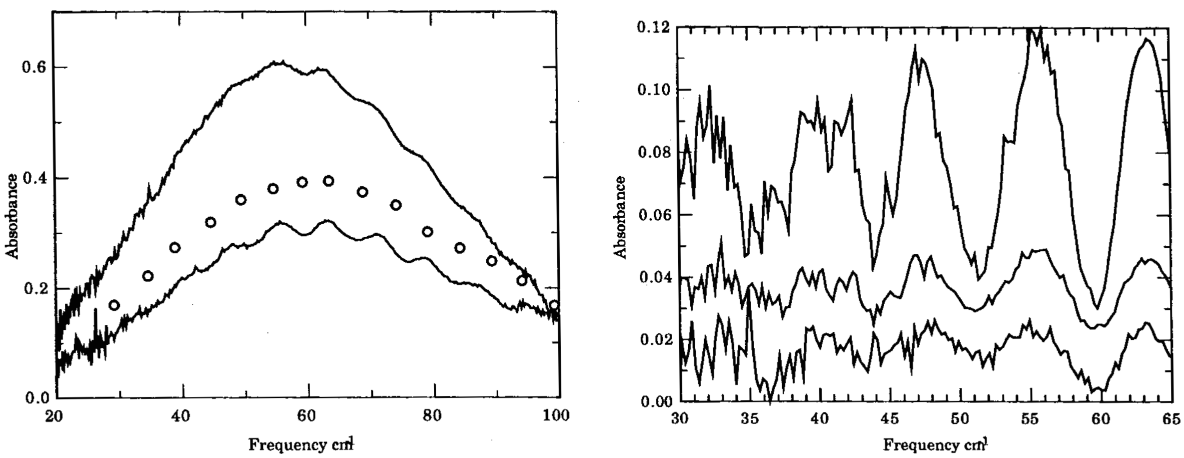

Fig. 1.— Left panel, low temperature N_2 and N_2-Ar spectra. The upper curve is from pure N_2 at 78 K, the circles are pure N_2 at 93 K, the lower curve is for a N_2-Ar mixture at 88 K; all densities are near 2.5 Amagat (see text). Right panel, baseline removed N_2 and N_2-Ar spectra. The upper curve is a 50/50 mix of N_2-Ar; the middle curve is a 24/76 mix of N_2-Ar; the lower curve is pure N_2. The curves are offset vertically by an arbitrary amount.

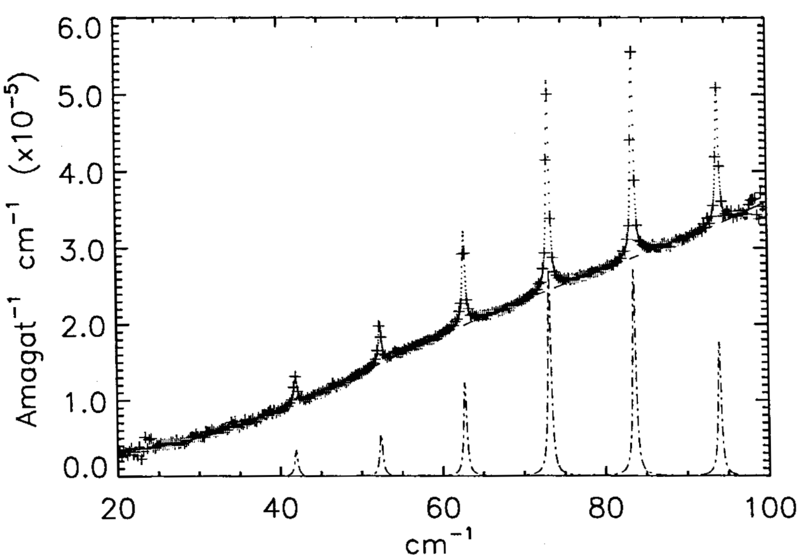

Fig. 2.— The absorption spectrum of methane. '+' are measurements of a 794 Torr methane sample at 113.5 K using a 60 m optical path. The dots are a fit to the data at 10x higher spectral resolution using 6 Lorentzian lines superposed on a quartic continuum; the dot-dash line shows the continuum removed spectrum.